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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY
MECHANISTIC INVESTIGATION OF THE ACENAPHTHENEQUINONE SENSITIZED--ETC(U)
AUG 78 G B SCHUSTER, J KOO

F/G 7/3

N00014-76-C-0745

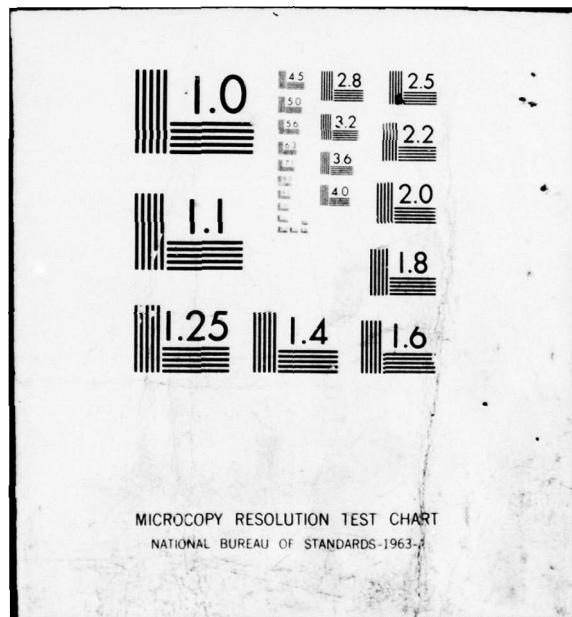
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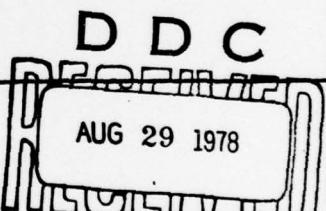
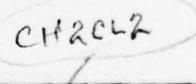


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REPORT DOCUMENTATION PAGE			READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER N0014-76-C-0745-16	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
TITLE (and Subtitle) Mechanistic Investigation of the Acenaphthene-quinone Sensitized Bartlett Photoepoxidation of Olefins. Concomitant Oxidation of the Sensitizer.		4. TYPE OF REPORT & PERIOD COVERED Technical	
AUTHOR(s) Gary B. Schuster and Ja-Young Koo		5. PERFORMING ORG. REPORT NUMBER 0	
PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Illinois Urbana, Illinois 61801		6. CONTRACT OR GRANT NUMBER(s) N0014-76-C-0745	
7. CONTROLLING OFFICE NAME AND ADDRESS Chemistry Program, Materials Science Division, Office of Naval Research, 800 N. Quincy Street, Arlington, VA 22217		8. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-051-616	
9. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		10. REPORT DATE August 22, 1978	
		11. NUMBER OF PAGES 24	
		12. SECURITY CLASS. (of this report) Unclassified	
		13a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
14. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release, Distribution Unlimited			
15. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 			
16. SUPPLEMENTARY NOTES  E			
17. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photooxidation Epoxide Singlet oxygen Quinone oxidation 			
18. ABSTRACT (Continue on reverse side if necessary and identify by block number) Photolysis of acenaphthenequinone in CH_2Cl_2 solution continuously saturated with oxygen generates 1,8-naphthalic anhydride in 80% isolated yield. When an olefin is included in the reaction solution it is converted to a mixture of oxidized products consisting mainly of allylic hydroperoxide and epoxide. It is demonstrated that the quantum efficiency for quinone oxidation is independent of quinone and olefin concentration. A mechanism is suggested for which an initial reaction between excited quinone and oxygen (cont.)			

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20. ^{of} results in covalent bond formation. Subsequent rearrangement of this intermediate accounts for the results observed.

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OFFICE OF NAVAL RESEARCH

Contract NO¹⁵ N0014-76-C-0745

Task No. NR-051-616

(9) TECHNICAL REPORT NO. N0014-76-C-0745-16

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by

(10) Gary B. Schuster and Ja-Young Koo

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Prepared for Publication

in

Journal of Organic Chemistry

School of Chemical Sciences

University of Illinois

Urbana, Illinois 61801

(11) 22 Aug 78

(12) 24P

August 22, 1978

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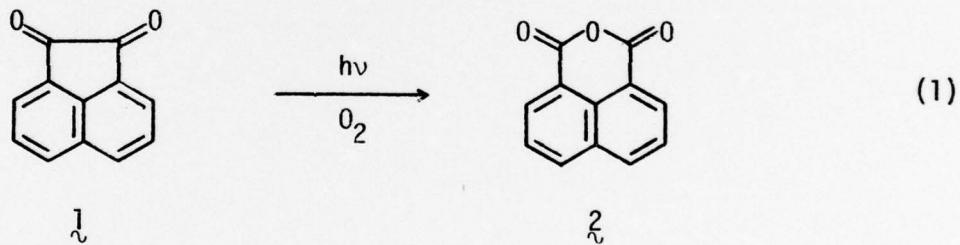
Abstract

Photolysis of acenaphthenequinone in CH_2Cl_2 solution continuously saturated with oxygen generates 1,8-naphthalic anhydride in 80% isolated yield. When an olefin is included in the reaction solution it is converted to a mixture of oxidized products consisting mainly of allylic hydroperoxide and epoxide. It is demonstrated that the quantum efficiency for quinone oxidation is independent of quinone and olefin concentration. A mechanism is suggested for which an initial reaction between excited quinone and oxygen results in covalent bond formation. Subsequent rearrangement of this intermediate accounts for the results observed.

The interaction of oxygen with electronically excited states of organic molecules can engender many interesting transformations. The most thoroughly studied of these processes is the reaction of a triplet excited state molecule (sensitizer) with oxygen to generate eventually singlet oxygen ($^1\text{O}_2$).² In recent years it has become apparent that for many photooxygenation reactions the generation of $^1\text{O}_2$ represents but a minor reaction path or plays a subsidiary or incidental role in the overall reaction. In a recent report Foote and coworkers³ suggest that 9,10-dicyanoanthracene sensitizes substrate oxidation through the intervention of superoxide radical anion (O_2^-). The O_2^- then proceeds to react with the radical cation of the substrate to form products reminiscent of $^1\text{O}_2$. Wilson and coworkers⁴ have found that photooxidation of cyclooctatetraene with p-benzoquinone as sensitizer leads to formation of 1,2,4-trioxanes. It is suggested that this reaction proceeds through a 1,4-biradical formed from the sensitizer and olefin. Interception of this intermediate by oxygen, it is postulated, generates the observed products. Shimizu and Bartlett⁵ have reported the results of their studies of photooxidation of olefins using α -dicarbonyl compounds as sensitizers. They find that olefins that normally are unreactive toward $^1\text{O}_2$ proceed to form high yields of epoxides (a product generally uncharacteristic of the reaction of $^1\text{O}_2$ with olefins). Bartlett⁶ has recently communicated the interesting observation that photoepoxidation under these conditions does not lead to the incorporation of an oxygen atom from molecular oxygen in the diketone sensitizer. This finding clearly eliminates many of the most straightforward paths for epoxide formation in this system. Jefford and Boschung⁷ have investigated the reaction of biadamantylidene with oxygen and a number of photosensitizers under a wide range of conditions. They report that

the mode of oxidation depends critically on the sensitizer. For example, in acetone solvent methylene blue sensitization results in the 1,2-dioxetane in greater than 95% yield; whereas with rose bengal as sensitizer epoxide is formed with a yield of greater than 95%. These workers conclude that at least two unconnected mechanisms are operating in this system. The first is the normal reaction of $^1\text{O}_2$ with olefins to form dioxetanes with a small amount of epoxide resulting, perhaps, from reaction of a perepoxide intermediate. The second is a complex path involving as a key step electron transfer from ground state sensitizer to $^1\text{O}_2$ to generate O_2^\cdot .

In this report we describe the results of our investigation of the auto-photoxidation of acenaphthenequinone (λ) to 1,8-naphthalic anhydride (γ) and the photooxidation of olefins using quinone λ as sensitizer. This system



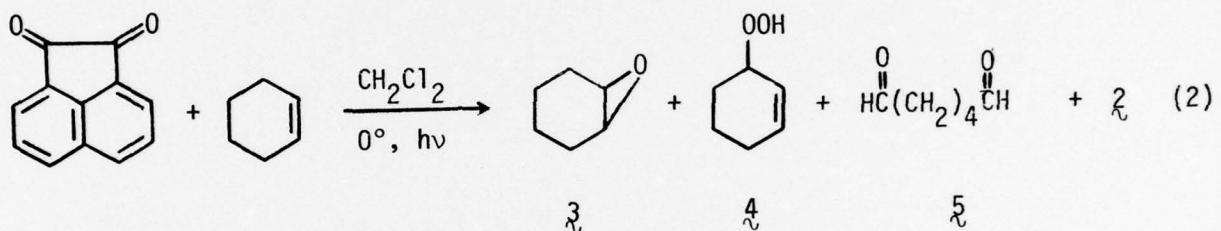
presents the opportunity to examine the disposition of oxygen in the reaction products and may provide further insight into the general structural and mechanistic requirements of photooxidation.

Results

Irradiation of a CH_2Cl_2 solution of quinone λ at 0° with a constant stream of oxygen flowing through the solution generates cleanly naphthalic anhydride γ as the only detected product.⁸ Anhydride γ can be isolated by evaporation of the solvent followed by recrystallization in 80% yield. This is similar

to the results reported by Mayuyama and coworkers⁹ who probed the photooxidation of I in THF solvent. We have determined that all three components, the quinone, light, and oxygen, are required for the reaction to proceed.

When quinone I was photooxidized in the presence of an olefin, cyclohexene for example, anhydride 2 was formed again and simultaneously the olefin was converted to a mixture of oxygenated products. For cyclohexene these were identified as: cyclohexene oxide (3), 3-hydroperoxycyclohexene (4) in 33 and 44% yield, respectively, and a small and variable amount of adipaldehyde (5).



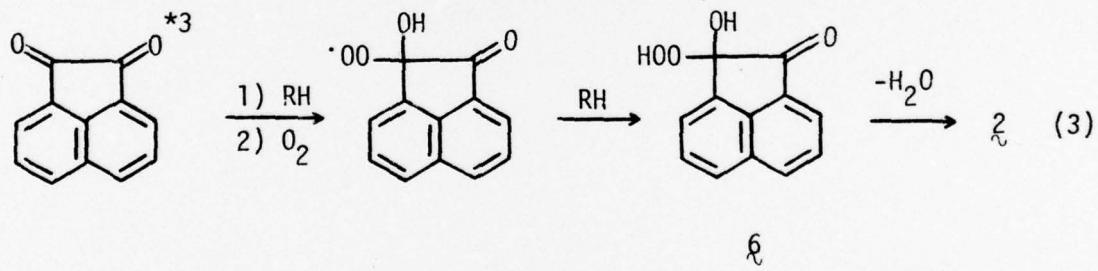
It was found again that quinone, light, and oxygen are required for the olefin oxidation.

A series of experiments was carried out to define the mechanism for these reactions. We first turn our attention to the oxidation of the quinone to the anhydride in the absence of olefin.

Investigation of the spectroscopic properties of quinone I revealed that in carefully purified CH_2Cl_2 at or below room temperature there is an emission with a maximum at 565 nm. This luminescence was identified as phosphorescence by the effect of added quenchers. For example, saturation of the solution with oxygen resulted in the complete quenching of this emission. Phosphorescence from quinone I has been observed in rigid media at 77°K to give approximately the same spectrum we observe in fluid solution.¹⁰ There is no detectable fluorescence from quinone I . We interpret this observation to indicate that the rate of intersystem crossing is rapid. Thus, the bimolecular chemistry of quinone I almost certainly originates from the triplet state.

The quantum yield for photooxidation of λ was determined under a variety of conditions by comparison with ferrioxalate.¹¹ These results are summarized in Table 1. Basically, it was observed that the efficiency of conversion of λ to anhydride γ is independent of the irradiating wavelength and, critically, also independent of the concentration of quinone λ . It is important to realize that the quantum yields were determined under conditions of low conversion so that competitive absorption by the product does not complicate the experiment.

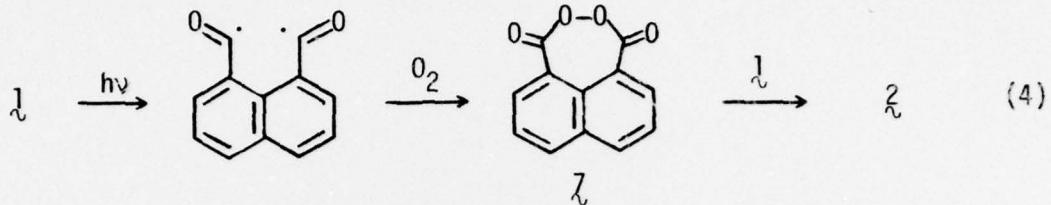
Several reactive intermediates can be imagined to precede formation of anhydride γ . Mayuyama and coworkers⁹ suggested that the initial step in the oxidation was hydrogen atom abstraction from solvent to form a radical intermediate which reacted sequentially with oxygen and a second hydrogen atom donor (solvent) to form hydroperoxy ketal δ . Loss of water from this intermediate, it was suggested, gives rise to the anhydride, eq. 3. To test



this mechanism we carried out the oxidation reaction in the presence of the very good hydrogen atom donor, 9,10-dihydroanthracene (DHA).¹² As can be seen from the data presented in Table 1, the addition of 1×10^{-3} M DHA did not result in a significant increase in the efficiency of photooxidation of λ . This observation, coupled with the observation of phosphorescence in CH_2Cl_2 , effectively rules out any mechanism which requires hydrogen atom transfer to be in competition with other fast unimolecular reactions under our conditions.

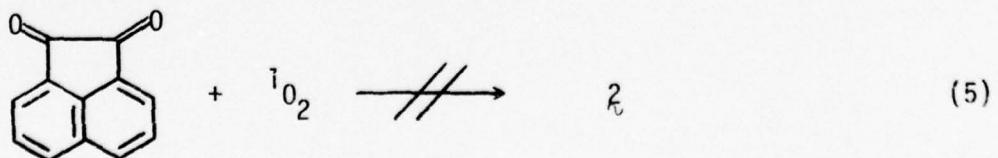
Another possible mechanism for the conversion of quinone λ to anhydride γ

is a Baeyer-Villiger type oxidation of the quinone by an intermediate diacylperoxide. The peroxide could be formed by the trapping of the biradical resulting from α -cleavage of the quinone with oxygen, eq. 4.¹³ To test



this possibility we sought to prepare and isolate peroxide γ by a series of different routes. Unfortunately, they were all spectacularly unsuccessful. However, we attempted to model the reaction of γ with λ by the use of phthaloyl peroxide (δ).¹⁴ Reaction of an equimolar solution of quinone λ and peroxide δ at room temperature for 12 h did not give rise to any anhydride ζ .

We expected that quenching of triplet λ by oxygen would give rise to some $^1\text{O}_2$. This expectation was borne out by experiment, see below. To examine the possibility that $^1\text{O}_2$ is responsible for the conversion of λ to ζ , we investigated the behavior of λ in the presence of $^1\text{O}_2$. Irradiation of methylene blue (MB) in the presence of oxygen has been shown to be an uncomplicated source of $^1\text{O}_2$.⁷ When a solution of λ and MB in CH_2Cl_2 is irradiated at wavelengths above 600 nm (only MB absorbs), no conversion to ζ is obtained. This finding clearly rules out the direct conversion of λ to ζ by $^1\text{O}_2$.



Another possible route for the conversion of λ to γ involves the generation of O_2^- by electron transfer from excited quinone. The oxidation potential of the quinone excited state is reduced by the amount of the excitation energy when compared to the ground state. Thus, electron transfer processes may compete effectively with other decomposition paths available to the excited state. Several diagnostic reagents have been developed to detect the presence of O_2^- in solution. Tetranitromethane reacts with O_2^- at nearly the diffusion limited rate to form NO_2 and the strongly absorbing nitroform anion.¹⁵ Nitrotetrazolium blue dication is reduced by O_2^- to form its highly colored diformazan.¹⁶ Incorporation of either of these indicators in solutions of quinone λ did not demonstrate the formation of O_2^- during irradiation. This finding, of course, does not rule out the possibility that a cage ion pair is formed which efficiently goes on to products. However, this result does indicate that free O_2^- is not involved in the oxidation of the added olefins; see below.

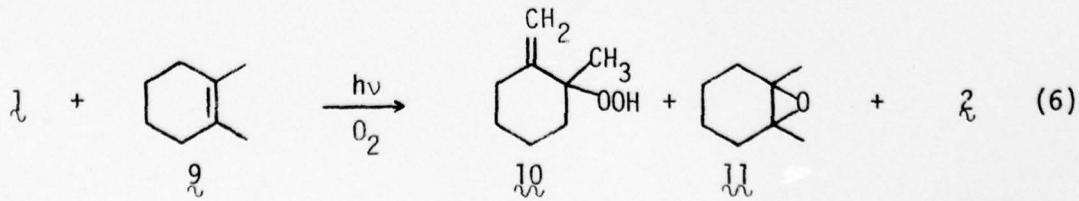
The concomitant oxidation of olefins during the conversion of λ to γ offers the opportunity to probe further the mechanism for the quinone oxidation and presents a system for the examination of the interaction of olefins with $n\pi^*$ type oxygen sensitizers. A series of experiments designed to define the transformations involved in this system was carried out.

The quenching of the phosphorescence of quinone by cyclohexene is a relatively inefficient process. We estimate that $k_{q\tau}$ (the Stern-Volmer slope) is approximately $410 M^{-1}$. Thus, cyclohexene competes only inefficiently with oxygen for the excited state of the quinone.¹⁷

As mentioned above, cyclohexene is converted to a number of oxidized products by the interaction with photoexcited λ and oxygen. The effect of

cyclohexene on the conversion of λ to anhydride κ was investigated. Surprisingly, over a range of cyclohexene concentration from ca. 4×10^{-3} to 5×10^{-1} M the quantum yield for the conversion of quinone λ to anhydride κ is completely unaffected by the olefin. Also, addition of 1,1-diphenylethylene does not quench the oxidation of λ . These data are collected in Table 1. The insensitivity of the oxidation of λ to the presence of olefin indicates that these two reaction paths do not diverge competitively from a common reactive intermediate.

To probe further the olefin oxidation reaction, this transformation was studied with several substrates under different conditions. Inclusion of the radical trap, 2,4,6-tri-*tert*-butylphenol in the reaction mixture did not change the product yields or ratios. This observation seems to rule out radical chain auto-oxidation. To confirm this conclusion the oxidation of 1,2-dimethylcyclohexene (g) was carried out. This system is particularly convenient because the 1O_2 and free radical oxidation products are different.¹⁸ Photolysis of a 3.4×10^{-3} M solution of g containing 3.4×10^{-3} M λ with light greater than 404 nm in CH_2Cl_2 at 0° gave rise to 2-hydroperoxy-2-methyl-1-methylenecyclohexylidene (10), dimethylcyclohexene oxide 11 , and anhydride κ in 70, 4, and 68% yield, respectively. Importantly, there is no evidence for formation of any 3-hydroperoxy-1,2-dimethylcyclohexene, the product of free radical oxidation of g . The oxidation of cyclohexene g under these conditions is apparently occurring by the reaction with 1O_2 to generate 10 and by some other path to form epoxide 11 .



To probe the stereochemistry of epoxide formation the oxidation of cis- and trans-stilbene was investigated. Photolysis of quinone λ in the presence of trans-stilbene under constant oxygen bubbling led to cis-stilbene, cis-stilbene oxide, trans-stilbene oxide, benzaldehyde, and anhydride ξ in 25, 4.6, 17, 10, and 60% yield, respectively, based on consumed trans-stilbene. Oxidation of cis-stilbene under the same reaction conditions led to an almost identical product mixture. Evidently there are at least four processes operating in this reaction system. The first is photosensitized trans to cis isomerization of stilbene. The triplet energy of the quinone dictates that the photostationary state from this reaction will contain predominantly the cis isomer.¹⁹ The second process is the oxidation of quinone to anhydride. The third is the reaction of 1O_2 with cis- or trans-stilbene to generate benzaldehyde.²⁰ The last is the formation of the stilbene oxides. This last reaction evidently is nearly completely non-stereoselective. Since starting with cis-stilbene gives the same ratio of oxides as starting with trans-stilbene, this observation indicates that the epoxidation of the olefins is most likely a stepwise process.

Discussion

Our investigation of these photooxidation reactions has revealed a quite complex system. Our findings do not lead to an inexorable mechanistic conclusion. However, it is clear that several possible mechanisms are not operating and we can propose a mechanism that is consistent with our experimental findings.

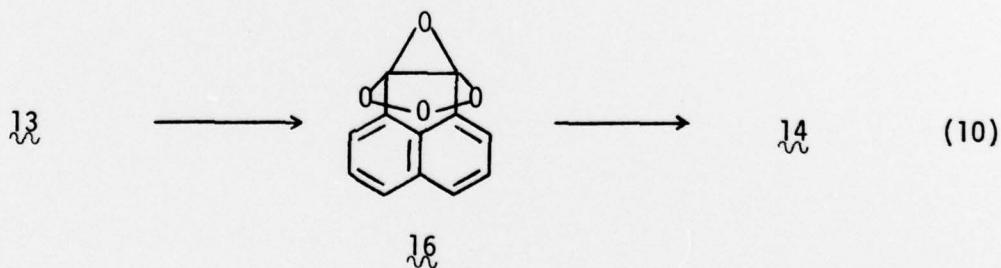
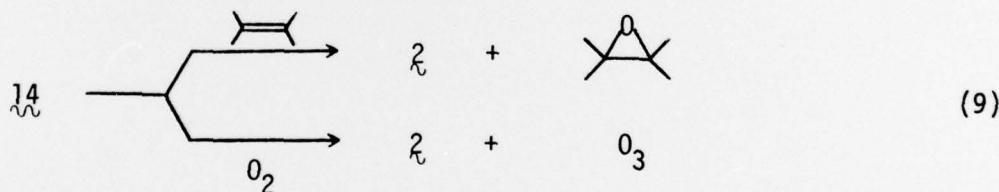
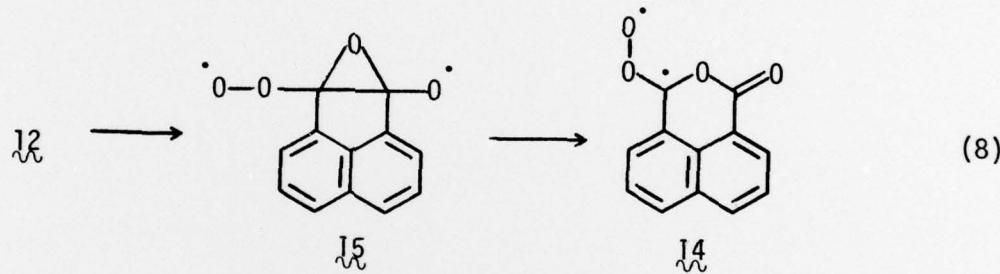
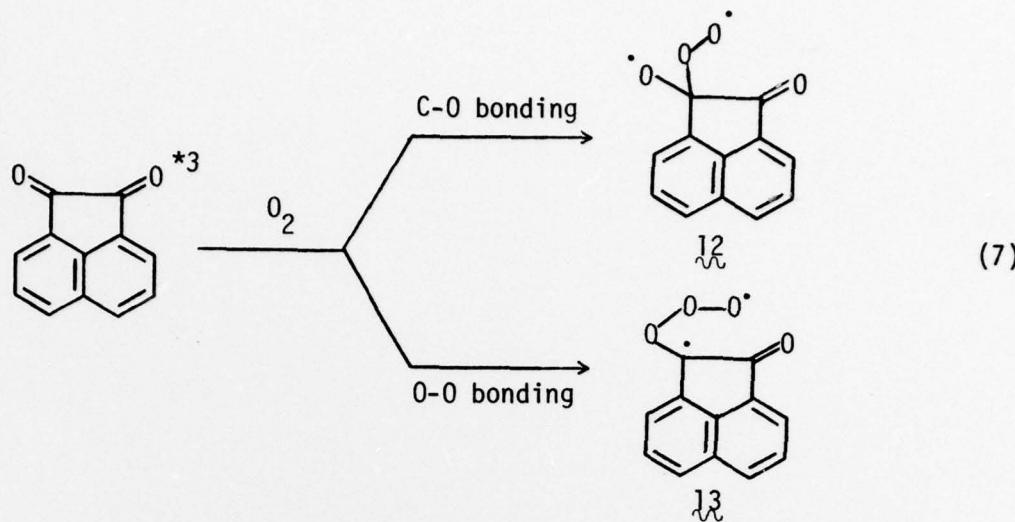
The most telling experiments are those that reveal the quantum efficiency for oxidation of λ to anhydride λ' to be independent of the quinone concentration and the presence of olefin. These findings indicate that only one quinone molecule is oxidized for every oxygen molecule consumed. If an oxidized intermediate was capable of converting a second quinone molecule to anhydride and also oxygenating olefin to epoxide, then the presence of olefin should have an inhibitory effect on the oxidation of quinone. Likewise, if an oxidized intermediate could either decay or transform a molecule of quinone to the anhydride, a dependence on quinone concentration would be expected. Moreover, these results indicate that the olefin competes only ineffectively with oxygen for the triplet excited state of the quinone as is evidenced by the relatively small value of $k_q\tau$.

We suggest that the initiating step in the reaction path leading to epoxide and quinone is bond formation between the excited quinone and oxygen. This step is potentially inconsistent with the $^{18}O - ^{18}O$ labeling results reported by Bartlett for oxidations with biacetyl and benzil.⁶ However, our system is perhaps different because we observe oxidation of the quinone whereas for the α -diketone systems, the sensitizer is recovered unchanged. We will attempt to explain this difference below.

A priori, there are two reasonable sites for oxygen bonding to excited quinone I_1 , the carbonyl carbon and the carbonyl oxygen. The detection of phosphorescence from I_1 at room temperature leads us to agree with the assignment of predominant $n\pi^*$ character for the lowest triplet of quinone I_1 .¹⁰ For $n\pi^*$ carbonyl compounds, the oxygen atom tends to be electrophilic while the π system behaves as a nucleophile.²¹ For this reason the initial reaction might be carbon oxygen bond formation to form the peroxy-alkoxy biradical intermediate I_2 . However, we cannot rule out, and tend to favor, formation of the trioxide biradical I_3 , eq. 7. Alkyl trioxides are in fact reasonably well characterized and have been detected in a number of systems.²² Indeed, an intermediate similar to trioxane I_3 is capable of explaining the labeling results reported by Bartlett if the active oxygen atoms are transferred one at a time to olefin molecules.

Whichever intermediate is in fact formed, our results indicate that it is not capable of oxidizing quinone to anhydride under our reaction conditions. Consider first the fate of I_2 . It is clear that this intermediate must at some time during the reaction insert one oxygen atom between the bridging carbons, and lose one oxygen atom. The sequence of these events is not revealed by our experiments. One reasonable possibility, however, is rearrangement of I_2 to what is essentially a carbonyl oxide, intermediate I_4 , eq. 8.

Attempts to trap this intermediate as an ozonide with added acetaldehyde were unsuccessful. Loss of oxygen from I_4 will yield the anhydride I_2 . In the presence of olefin, the active oxygen of I_4 would be transferred to form the epoxide. This reaction is expected to be non-stereospecific if the biradical rather than the zwitterionic form of I_4 is the major contributor. Moreover, oxygen atom transfers of this type have



been postulated to occur from the peroxide intermediates formed during ozonolysis of alkynes.²³ In the absence of olefin, loss of oxygen from J_4 does not oxidize a second quinone. One possible pathway is the donation of an oxygen atom from J_4 to an oxygen molecule to generate ozone, eq. 9.

While we have no direct evidence for the formation of ozone, it is interesting to note the formation of adipaldehyde from the cyclohexene oxidation, a product not reported to result from the reaction of ${}^1\text{O}_2$ with this olefin, but one that is expected to result from the ozonolysis.²⁴ Moreover, this product is observed only at low olefin concentration where competition between epoxide formation and generation of ozone might permit the latter reaction to occur.

Finally, it should be noted that a similar reaction sequence can be postulated if trioxide intermediate J_3 results from the interaction of excited J with oxygen. However, in this case intermediate J_6 (analogous to J_5) would undergo two bond cleavage to form J_4 , eq. 10. The rearrangement of J_6 to J_4 is exactly the well preceded reaction of a primary ozonide to the Criegee intermediate.²⁵

Competing with the oxidation of triplet J is energy transfer to ground state oxygen to form ${}^1\text{O}_2$. In the absence of olefin the ${}^1\text{O}_2$ returns to the ground state and this path simply represents a route for energy wastage. In the presence of olefin the ${}^1\text{O}_2$ reacts to form primarily the hydroperoxide products observed.

One final point to be discussed is the relationship of this system and proposed mechanism to that discovered by Bartlett and coworkers.⁵ The major difference is the fate of the sensitizer. It is tempting to speculate that, at least for benzil and biacetyl sensitizers, the trioxide intermediate analogous to J_3 is formed exclusively. As

mentioned above, it is possible that this type of intermediate can explain the labeling study. The question that remains to be answered concerns the lack of cyclization of these intermediates to analogues of 16 . The most reasonable explanation centers on the constrained five-membered ring of 13 . Perhaps entropic factors mitigate against rapid cyclization in the acyclic cases and, at high olefin concentration, oxygen atom transfer to form epoxide occurs exclusively.

In summary, the reaction sequence outlined in equations 7, 8, 9 and 10 represents a plausible sequence of events for the oxidation of 1 and olefins that is consistent with the known experimental observations. Further work on this apparently general photooxidation scheme is underway.

Experimental

General. All melting points were corrected according to the melting point (80.1°C) of sublimed naphthalene. NMR spectra were recorded on a Varian Associates EM-390 instrument with tetramethylsilane internal standard. Gas chromatographic analysis was carried out on a Varian Associates 2700 all glass chromatograph with a $6' \times 1/4"$, 3% SE-30 column. Absorption spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer or on a Cary 14 instrument. Emission spectra were recorded on a Farrand Mark I spectrofluorimeter. Irradiation was carried out on a preparative scale using an Hanovia 450 W medium pressure Hg arc lamp cooled in a water jacketed Pyrex® well. The well was covered with tape to block light emission over all but an approximately 1 inch opening. Wavelength selection was achieved by placing the appropriate Corning color glass filter in the light path. The light was then focused on the reaction vessel which was maintained at constant temperature by means of an external cooling source. Irradiation on an analytical scale was carried out using the excitation optics of the Farrand spectrofluorimeter. Wavelength selection was achieved with the excitation monochromator with 10 nm bandpass slits in both the entrance and exit ports. The concentration of anhydride $\frac{2}{\lambda}$ was monitored spectroscopically at 340 nm a wavelength at which the quinone λ is nearly transparent.

Purification of acenaphthenquinone (λ). Technical grade quinone (Aldrich Chemical Company) was purified by chromatography on Silica Gel with CH_2Cl_2 followed by repeated recrystallization from CH_2Cl_2 to give long yellow needles (mp 250-253 with decomposition). The best criterion for purity was the phosphorescence emission spectrum in CH_2Cl_2 at room temperature. In general, samples of λ were recrystallized until further

recrystallization led to no further changes in the intensity of the phosphorescence.

Photolysis of Quinone 1 a) In the absence of olefin. A solution of quinone (50 mg, 0.28 mmol) in 100 mL of freshly distilled CH_2Cl_2 was prepared and purged with O_2 at 0° . The solution was irradiated as described above using a CS-3-73 filter with constant O_2 bubbling for 4h. Evaporation of the solvent in vacuo gave a solid which was recrystallized from CH_2Cl_2 to give 43 mg (80%) of an off-white solid identified as 1,8-naphthalic anhydride by comparison with an authentic sample (Aldrich Chemical Company).

b) With cyclohexene. A solution of 1 (42 mg, 0.2 mmol) and freshly distilled cyclohexene (19 mg, 0.23 mmol) was prepared in 60 mL of CH_2Cl_2 . The solution was irradiated as described in part a above for 5.5h. Analysis of the photolysis solution by gas chromatography revealed cyclohexene oxide (33%, by comparison with an authentic sample). Analysis of the NMR spectrum revealed hydroperoxide 4 in ca. 40% yield identified by comparison with an authentic sample²⁴ and adipaldehyde.²⁵ Evaporation of the solvent and crystallization gave anhydride 2 in 65% isolated yield. An identical experiment, except that 2,4,6-tri-tert-butyl phenol (2.99 mg, 0.011 mmol) was included in the photolysis solution, gave the same product mixture.

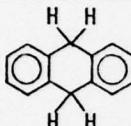
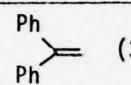
c) With 1,2-dimethylcyclohexene (9). The dimethylcyclohexene was prepared by the procedure of Signaigo²⁷ and purified by preparative gas chromatography. A solution of 1 (49.5 mg, 0.27 mmol) and 9 (30 mg, 0.272 mmol) was prepared in 60 mL of CH_2Cl_2 and irradiated for 5h as described above. Gas chromatographic analysis of the reaction solution revealed epoxide 11 in 4% yield (based on starting 9). Analysis by NMR showed a 70% yield of

hydroperoxide λ . Neither NMR nor GC analysis showed any evidence for 3-hydroperoxy-1,2-dimethylcyclohexene. We estimate we could have detected 2% of this compound. Evaporation of the solvent and crystallization gave γ in 68% yield (based on λ).

d) With trans-stilbene. A solution of λ (43 mg, 0.23 mmol) and trans-stilbene (41.5 mg, 0.23 mmol) in 40 mL of CH_2Cl_2 was irradiated as above. The following products were identified and quantitated by gas chromatographic comparison with authentic samples (yields are based upon starting trans-stilbene): cis-stilbene, 25%; cis-stilbene oxide, 4.6%; trans-stilbene oxide, 17%; benzaldehyde, 10%. Evaporation of the solvent and crystallization gave anhydride γ in 60% yield. In an experiment with cis-stilbene (44 mg, 0.24 mmol), a virtually identical mixture of products was obtained.

Acknowledgement. This work was supported in part by the Office of Naval Research, in part by the Petroleum Research Fund administered by the American Chemical Society, and in part by the National Science Foundation.

Effect of Concentration, Wavelength, and Quenchers
on the Photooxidation of λ to Anhydride $\tilde{\lambda}$.^a

$[\lambda]$	Additive	Irradiating Wavelength (nm)	Φ_{ox}^{rel} ^b
8.8×10^{-5}	—	315	1.00
1.04×10^{-4}	—	483	0.82
1.04×10^{-4}	 (1.16×10^{-3} M)	410	0.97 ^c
1.04×10^{-4}	 (3×10^{-3} M)	483	0.92
2.64×10^{-5}	—	315	0.93
6.59×10^{-5}	—	315	1.11
1.32×10^{-4}	—	315	0.97
2.64×10^{-4}	—	315	1.10
5.27×10^{-4}	—	315	1.00
2.81×10^{-3}	 (3.95×10^{-3} M)	380	1.00 ^d
2.81×10^{-3}	 (1.98×10^{-2} M)	380	0.95
2.81×10^{-3}	 (9.88×10^{-2} M)	380	1.06
2.81×10^{-3}	 (4.94×10^{-1} M)	380	1.00

^aIrradiations were carried out with a 150W Hg-Xe lamp with a 0.25 M monochromator used for wavelength selection. Bandpass was adjusted to be 10 nm of the central wavelength stated in the table.

^bThe absolute quantum yield for photooxidation was determined at 315 and 483 nm to be 0.087 and 0.071, respectively, by comparison with ferrioxalate at 0° in CH_2Cl_2 with $[\lambda] = 8.8 \times 10^{-5}$ M.

^cRelative to irradiation of an identical solution of λ at 410 nm but without the addition of the dihydroanthracene.

^dRelative to irradiation of an identical solution of λ at 380 nm but without the addition of cyclohexene.

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